Supporting Information for:

Kinetic Modeling of 1-Hexene Polymerization

Catalyzed by Zr(tBu-ON\textsubscript{2}NMe\textsubscript{2}O)Bn\textsubscript{2}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}

Jeffrey M. Switzer,† Nicholas E. Travia,‡ D. Keith Steelman,‡ Grigori A. Medvedev,† Kendall T. Thomson,† W. Nicholas Delgass,† Mahdi M. Abu-Omar,‡* and James M. Caruthers†*

†School of Chemical Engineering and ‡Dept. of Chemistry, Purdue University, West Lafayette, Indiana 47907

S1. Data Error Analysis .............................................................................................................................................. 2
S2. Kinetic Model Equations ....................................................................................................................................... 5
S3. Equal Importance Weighting Scheme .................................................................................................................. 7
S4. Rate Constant Approximation .......................................................................................................................... 8
S5. Analysis of Reinitiation Mechanism .................................................................................................................. 11
S6. Modeling of Additional Data .......................................................................................................................... 13
S7. Catalyst Activation ............................................................................................................................................... 17
S8. Kinetic Modeling with 100% Catalyst Participation ........................................................................................ 19
S9. Kinetic Modeling without Recovery Pathway .................................................................................................. 21
S10. Mechanism with Monomer-Dependent Vinylene Formation ........................................................................... 22
**S1. Data Error Analysis**

In a typical experiment, the reproducibility of the data is determined through repeat trials. An average value and a standard deviation can be calculated when the experimental conditions are identical. However, in the experiments in this report we have hypothesized that during the experiment the catalyst concentration is not equal to the measured precatalyst concentration, and the actual amount may not be consistent from one trial to the next even when the same precatalyst amount has been measured. It does not make sense to compute an average value or standard deviation of a measurement in this case because the value for each repeat can be expected to differ. However, the objective function used to optimize the data requires that the standard deviation be known for each set of data, and so some method of determining the error in the data is needed.

Two methods have been identified that can be used to determine an error range for the data measurements: propagation of measurement error and error as determined through the method of standard additions. These methods are discussed below. Once both error values have been calculated for each data response, the larger of the two is used as an approximation of the standard deviation that would have resulted from repeated trials.

The error bars shown in Figure 1 represent a 95% confidence interval for each data point as determined by the Student’s t-distribution with the standard deviation replaced by its approximation. Additionally, the standard deviations required to solve the objective function have been replaced with this approximation.

**Propagation of Measurement Error.** Several measurements are necessary to calculate the monomer, vinyl, and active site concentrations, and each measurement has some uncertainty due to the precision of the measurement instrument. Although this type of error does not address the reproducibility of the data, it can be thought of as a lower bound for the standard deviation—
even if repeated measurements were highly reproducible, their accuracy is limited by the precision with which the values were measured, and the actual average may still vary within the measurement error range. First, the propagation of measurement error method in the context of this work will be discussed.

Given an equation \( F = f(a, b, c, \ldots) \) in which the parameters are uncorrelated, the measurement error \( \sigma_F \) is calculated with the following equation:

\[
\sigma_F^2 = \left( \frac{\partial F}{\partial a_{b,c,\ldots}} \right)^2 \sigma_a^2 + \left( \frac{\partial F}{\partial b_{a,c,\ldots}} \right)^2 \sigma_b^2 + \left( \frac{\partial F}{\partial c_{a,b,\ldots}} \right)^2 \sigma_c^2 + \ldots \tag{S1}
\]

where \( \sigma_i \) represents the error in the measurement of parameter \( i \).

The equation used to calculate vinyl and active site concentrations was:

\[
[X] = \frac{A_p \times [I,S] \times \frac{V_{NMR}}{V_{sample}}}{1 - \left( \frac{V_{meth} + \frac{d}{d_{tol}}} {V_{flask}} \right)} \tag{S2}
\]

The variables in Equation S2 are provided in Table S1. The equation used to calculate monomer consumption was:

\[
\frac{[M]}{[M]_0} = \frac{A_p \times \frac{V_f}{V_i}}{A_0 \times \frac{V_f}{V_i} \left( 1 - \frac{V_{meth} + \frac{d}{d_{tol}}} {V_{flask}} \right)} \tag{S3}
\]

The variables in Equation S3 are provided in Table S2.
Table S1. Variables and errors used to calculate vinyl and active site concentrations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Identity</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_p$</td>
<td>Area under desired NMR peak</td>
<td>0.005</td>
</tr>
<tr>
<td>[I.S.]</td>
<td>Concentration of internal standard</td>
<td>0.05  mM</td>
</tr>
<tr>
<td>$V_{NMR}$</td>
<td>Volume of analyzed sample after dilution</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$V_{sample}$</td>
<td>Volume of analyzed sample before dilution</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$V_{meth}$</td>
<td>Volume of methanol used to quench</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$d$</td>
<td>Drops of toluene to fill quenching flask</td>
<td>1     drop</td>
</tr>
<tr>
<td>$d_{tol}$</td>
<td>Drops of toluene per unit volume</td>
<td>1     drop mL$^{-1}$</td>
</tr>
<tr>
<td>$V_{flask}$</td>
<td>Volume of quenching flask</td>
<td>0.02  mL</td>
</tr>
</tbody>
</table>

Table S2. Variables and errors used to calculate vinyl and active site concentrations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Identity</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_p$</td>
<td>Area under NMR peak after quench</td>
<td>0.05</td>
</tr>
<tr>
<td>$A_o$</td>
<td>Area under NMR peak before reaction</td>
<td>0.05</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Batch volume after catalyst is added</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$V_i$</td>
<td>Batch volume before catalyst is added</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$V_{meth}$</td>
<td>Volume of methanol used to quench</td>
<td>0.02  mL</td>
</tr>
<tr>
<td>$d$</td>
<td>Drops of toluene to fill quenching flask</td>
<td>1     drop</td>
</tr>
<tr>
<td>$d_{tol}$</td>
<td>Drops of toluene per unit volume</td>
<td>1     drop mL$^{-1}$</td>
</tr>
<tr>
<td>$V_{flask}$</td>
<td>Volume of quenching flask</td>
<td>0.02  mL</td>
</tr>
</tbody>
</table>

**Error from Standard Additions Method.** The method of standard additions was used to collect vinyl and active site data. Samples were prepared for NMR analysis with an aliquot of a standard, and Equation S2 was used to determine the concentration of the species. Then an additional aliquot of the standard was introduced, and the measurement was repeated. In theory, this procedure can be repeated as many times as desired, but in this work three measurements were deemed sufficient.
In the case of the monomer consumption data a different method was used. For each sample to be analyzed the olefinic hydrogen peaks were measured via NMR, resulting in two peaks, both of which can be used to calculate the monomer concentration using Equation S3.

Although the actual experiment is not repeated, this method produces a population of values representing the same quantity for which a mean and standard deviation can be computed. In this case, the significance of the standard deviation is that it quantifies the precision of the NMR equipment, and the value can serve as another lower bound on the standard deviation that would come from true experimental repeats.

**S2. Kinetic Model Equations**

The mechanism from Scheme 2, which was used to fit the data in this report, can be presented as a series of chemical reactions. These reactions are given below.

**List of Species**

- **C** Precatalyst
- **A** Activator
- **C** Activation

**List of Reactions**

\[ C + A \xrightarrow{k} C^* \]  
Catalyst Activation  \((S4)\)
C* + M $\xrightarrow{k_i} R_1$ \hspace{1cm} \text{Initiation} \hspace{1cm} (S5)

R_n + M $\xrightarrow{k} R_{n+1}$, \hspace{1cm} 1 $\leq$ n $\leq$ L_{max} \hspace{1cm} \text{Normal Propagation} \hspace{1cm} (S6)

R_n + M $\xrightarrow{k_{mic}} P_{n+1}$, \hspace{1cm} 1 $\leq$ n $\leq$ L_{max} \hspace{1cm} \text{2,1-Misinsertion of Monomer} \hspace{1cm} (S7)

P_n + M $\xrightarrow{k_{mic}} R_{n+1}$, \hspace{1cm} 2 $\leq$ n $\leq$ L_{max} \hspace{1cm} \text{Recovery of Normal Catalyst Site} \hspace{1cm} (S8)

R_n $\xrightarrow{k_{vinylidene}} C^*_{HI} + SR_n$, \hspace{1cm} 1 $\leq$ n $\leq$ L_{max} \hspace{1cm} \text{Vinylidene-forming $\beta$-Hydride Formation} \hspace{1cm} (S9)

P_n $\xrightarrow{k_{vinylene}} C^*_{HI} + SP_n$, \hspace{1cm} 2 $\leq$ n $\leq$ L_{max} \hspace{1cm} \text{Vinylene-forming $\beta$-Hydride Formation} \hspace{1cm} (S10)

C^*_{HI} + M $\xrightarrow{k_{re-irritation}} R_1$ \hspace{1cm} \text{Initiation of Metal-Hydride} \hspace{1cm} (S11)

In these reactions, L_{max} represents the maximum number of monomers in the polymer chains.

The value of this parameter must be set sufficiently high to account for all polymer chains in the experiments, and it is typically set around 20% higher than the value determined from the highest molecular weight seen in the MWDs.

This mechanism results in a set of ordinary differential equations (ODEs) that can be solved to determine the time dependent concentration of each of the chemical species for a given set of rate constants. These calculated concentrations are compared to the data using the objective function, and a Levenberg-Marquardt optimization routine is used to adjust the rate constants so as to minimize the objective function. The ODEs are listed below.

\textbf{List of ODEs}

\[
\frac{d[C]}{dt} = -k_a [C][A] \hspace{1cm} (S12)
\]

\[
\frac{d[A]}{dt} = -k_a [C][A] \hspace{1cm} (S13)
\]

\[
\frac{d[C^*]}{dt} = k_a [C][A] - k_i [C^*][M] \hspace{1cm} (S14)
\]
\[
\frac{d[M]}{dt} = \left( -k_i[C^*] - (k_p + k_{\text{mis}} \sum_{n=1}^{L_{\text{max}}} [R_n]) - k_{\text{rec}} \sum_{n=2}^{L_{\text{max}}} [P_n] \right) - k_{\text{re-initiation}} [C^*] [M] \]  
(S15)

\[
\frac{d[R_1]}{dt} = \left( k_i[C^*] - k_p [R_1] - k_{\text{mis}} [R_1] + k_{\text{re-initiation}} [C^*] [M] - k_{\text{vinyldene}} [R_1] \right) \]  
(S16)

\[
\frac{d[R_n]}{dt} = \left( k_p ([R_{n-1}] - [R_n]) - k_{\text{mis}} [R_n] + k_{\text{rec}} [P_{n-1}] [M] - k_{\text{vinyldene}} [R_n] \right) 2 \leq n \leq L_{\text{max}} \]  
(S17)

\[
\frac{d[P_n]}{dt} = \left( k_{\text{mis}} [R_{n-1}] - k_{\text{rec}} [P_n] [M] - k_{\text{vinylene}} [P_n] \right) 2 \leq n \leq L_{\text{max}} \]  
(S18)

\[
\frac{d[C^*]}{dt} = \left( -k_{\text{re-initiation}} [C^*] [M] + k_{\text{vinyldene}} \sum_{n=1}^{L_{\text{max}}} [R_n] \right) + k_{\text{vinylene}} \sum_{n=2}^{L_{\text{max}}} [P_n] \]  
(S19)

\[
\frac{d[SR_n]}{dt} = k_{\text{vinyldene}} [R_n] 1 \leq n \leq L_{\text{max}} \]  
(S20)

\[
\frac{d[SP_n]}{dt} = k_{\text{vinylene}} [P_n] 2 \leq n \leq L_{\text{max}} \]  
(S21)

It is assumed that the activation step occurs instantaneously; thus, Equations S12, S13, and the first term in Equation S14 are ignored. The remaining equations are solved simultaneously with all initial concentrations set to zero except the monomer concentration and \( C^* \), which is set equal to the initial precatalyst concentration times a multiplier parameter. This multiplier is constrained from zero to one, and it represents the fraction of precatalyst that participates in the reaction as active catalyst.

**S3. Equal Importance Weighting Scheme**

The weighting parameter in the optimization objective function allows the researcher to give a quantitative amount of importance to specific experimental results. If the data have no error and the model is completely accurate, then the optimized parameters should be independent of the weighting scheme chosen. Novstrup et al. used different weighting schemes to show that their
results were not largely affected by changing the weighting scheme, \(^1\) signifying that no single data response is influencing the results more than the others. However, in this report the weighting scheme is used for the opposite purpose; we believe that certain data responses are more important than others, and we want to optimize the model parameters with this in mind.

To determine an appropriate weighting scheme, the Trial 1 data (red) from Figure 1 is used. The results from weighting each data response equally, shown in Figure S1, are instructive. The model prediction of the MWD at 65 s displays a sharp high MW tail, which is in contrast to the data. While the overall sum of squares error is minimized, the prediction of this data is qualitatively incorrect. To improve the fit, the weight we assign this data response can be increased for subsequent optimization, recognizing that matching the tails of this distribution is necessary in order to arrive at an adequate solution. The active site data were also given additional weighting to improve the model fit of these data. Several weighting values were tried until a satisfactory set was found. The value of the weighting factor was increased from 1 to 10 for the previously specified data responses. The resulting model prediction is detailed in the text and results in the fits in Figure 1.

**S4. Rate Constant Approximation**

Recognizing that the system of equations in this problem is non-linear, it is to be expected that the objective function may have several local minima. Before optimization is performed it is important to find a good set of initial guesses for the rate constants. This can be done with a guess-and-check methodology, but the parameter space is very large. It is much more effective to analyze the data responses and develop the initial rates one at a time, if possible. Such a method is described next.
Figure S1. Model prediction of the Trial 1 data from Figure 1. Red lines represent the model generated by optimizing the rate constants in Scheme 2 against equally weighted data responses. (a) MWD data. (b) Monomer consumption. (c) Vinyl concentration. (d) Active site concentration. Line and point styles represent the same as in Figure 1.

First, a representative set of data is chosen, e.g. the red data from Figure 1. Starting with the observation from the active site data that only about 45% of the precatalyst is responsible for all polymer chains produced and noting that the slope of the monomer consumption data is determined primarily from the concentration of active catalyst and $k_p$, a preliminary value of $k_p = 7 \text{ M}^{-1} \text{s}^{-1}$ is assigned. However, in the candidate model only the catalyst with normally inserted polymer can be considered as active catalyst. Since during the experiment approximately 70% of the active sites are primary sites, the preliminary $k_p$ value is only about 70% of the true value, yielding $k_p = 10 \text{ M}^{-1} \text{s}^{-1}$.

Data from low M:C experiments offer the best insight into $k_i$. Therefore the data in Figure 2 are used to devise a preliminary guess. Assuming a value of $k_p = 10 \text{ M}^{-1} \text{s}^{-1}$, and also assuming that ~45% of the catalyst is active, a simpler mechanism of initiation and propagation only is
used to search for the best value of $k_i$. A value of $k_i = 0.3 \text{ M}^{-1} \text{ s}^{-1}$ was found to fit the data reasonably well.

To determine the initial values of the chain transfer rate constants, $k_{\text{vinylidene}}$ and $k_{\text{vinylene}}$, it should first be noted that the data show nearly constant active site concentrations after the earliest data point and nearly linear vinyl formation. Because the model predicts a monomer independent chain transfer pathway, the slope of the vinylidene formation curve is determined directly from the primary active site concentration and $k_{\text{vinylidene}}$. The result is a value of $k_{\text{vinylidene}} = 0.015 \text{ s}^{-1}$. A similar argument for vinylene uses the secondary active site concentration and results in a value of $k_{\text{vinylene}} = 0.010 \text{ s}^{-1}$.

The misinsertion and recovery rate constants, $k_{\text{mis}}$ and $k_{\text{rec}}$ respectively, are more difficult to estimate because changes to these rates affect the model in several ways. To develop an initial approximation, the active site data should be examined. In the secondary active site data, there is a buildup of sites followed by a decrease. The observed decrease late in the reaction is expected for monomer dependent secondary site formation because less monomer is present. The slow increase towards the maximum can best be explained by a slow $k_{\text{mis}}$ compared to $k_p$, although it will also be seen for low $k_i:k_p$ ratios. By setting $k_{\text{rec}}$ to zero, a reasonable fit of the active site data can be obtained when $k_{\text{mis}} = 0.04 \text{ M}^{-1} \text{ s}^{-1}$. These values were used as a starting point for optimization.

The $k_{\text{reinitiation}}$ rate constant can also be approximated. A small $k_{\text{reinitiation}}:k_p$ ratio would result in a decrease in the rate of monomer consumption and vinyl group formation as well as a decrease in both primary and secondary active site concentrations late in the reaction. Absence of these trends means that $k_{\text{reinitiation}}$ is comparable in value to $k_p$. The data show a constant amount of
primary active sites and a constant rate of formation of vinyl groups. Therefore \( k_{\text{reinitiation}} = k_p \) is a reasonable initial approximation.

These initial values of the rate constants have been chosen to be consistent with the monomer consumption data, the vinyl data, and the active site data. The model prediction using these rate constants appears in Figure S2. While the model predicts the data in Figures S2b-d well, the MWDs of Figure S2a are not well-predicted, particularly the two higher MW distributions. Clearly, either the mechanism or the rate constants are not correct, and only with the introduction of MWD data is this known.

Thus far the MWD data has not been used in the estimation of the rate constants. This additional data will either support or refute the proposed mechanism, and given that the data support the mechanism, they provide the ability to more accurately quantify the rate constants. In order to claim that a reliable model has been generated, that model must fit all the available data, including the MWDs, and in order to fit the MWDs they must be included in the objective function. A stepwise procedure of rate constant assignment will not suffice.

**S5. Analysis of Reinitiation Mechanism**

In the analysis of the catalyst system, two rate constants have been ignored on the basis that the data can be predicted independent of the value of the associated rate (within certain constraints). One of these is the rate of catalyst activation, which has been assumed to be sufficiently fast that the amount of precatalyst can be set equal to the amount of activated catalyst times a multiplication factor as an initial condition.
Figure S2. Model prediction of the Trial 1 data of Figure 1. Red lines represent a model where all parameters from Scheme 2 are approximated without using the MWDs. (a) MWD data. (b) Monomer consumption. (c) Vinyl concentration. (d) Active site concentration. Line and point styles represent the same as in Figure 1.

The other rate that has been ignored is the reinitiation rate, which governs how fast a catalyst can begin to grow a new chain following chain transfer. Because this rate influences only a single monomer insertion (compared with \( k_p \), which governs many monomer insertions), any value of \( k_{\text{reinitiation}} \) greater than \( k_p \) will cause no significant change to the model from the case where \( k_{\text{reinitiation}} = k_p \). On the other hand, when \( k_{\text{reinitiation}} \) is much less than \( k_p \), a clear effect should be seen in the monomer consumption and active site data because following chain transfer the catalyst will become trapped in a state where it is unable to polymerize. What this means is that if \( k_{\text{reinitiation}} \) is small we should be able to determine its value, but if \( k_{\text{reinitiation}} \) is large we have no way to give it a precise value.

We wish to determine the range of \( k_{\text{reinitiation}} \) over which the model prediction of the data is not affected. To this end, the data from one of the trials reported in Figure 1 is modeled with
differing values of $k_{\text{reinitiation}}$, as shown in Figure S3. When defined as a parameter in the objective function, $k_{\text{reinitiation}}$ for this trial is optimized to 1.4 M$^{-1}$ s$^{-1}$. However, if $k_{\text{reinitiation}}$ is constrained to 20 or 100 M$^{-1}$ s$^{-1}$ and the other rates optimized with this constraint, the resulting model predictions are nearly identical with little change to the optimized values of the other parameters.

**S6. Modeling of Additional Data**

Several experiments were performed and analyzed beyond the initial experiments reported in Figure 1. The purpose of these data sets was to validate the mechanism and rate constants that were reported in Table 2.

Figure S4 shows data from several experiments performed at the same initial conditions as those in Figure 1. The black data represents an experiment performed in an NMR tube, while the rest of the data represent experiments performed as larger batch scale reactions. The purple data, also appearing in Figure 3, show a higher rate of reaction, which is consistent with the observation that the active site concentration is larger than in the initial data set (Figure 1).

The data in Figure S5, collected at identical initial concentrations, can be fit by the model parameters in Table 2, but with 43% of the precatalyst participating in the reaction. The late reaction molecular weight peak shows the best agreement, while the error in the remaining peaks can be explained by the deficiencies of the GPC with respect to low MW polymer. Another experiment at these initial conditions produced MWDs and vinyl concentration data. The proposed mechanism and optimized rate constants provide a very good fit with 47% of the precatalyst participating (Figure S6).
Figure S3. Model predictions of the Trial 2 data from Figure 1. The line colors represent model predictions with all rate constants from Scheme 2 optimized except for $k_{\text{reinitiation}}$. Red: $k_{\text{reinitiation}} = 1.4 \ \text{M}^{-1} \ \text{s}^{-1}$; Green: $k_{\text{reinitiation}} = 20 \ \text{M}^{-1} \ \text{s}^{-1}$; Blue: $k_{\text{reinitiation}} = 100 \ \text{M}^{-1} \ \text{s}^{-1}$. Note that blue overlaps green extremely closely. (a) MWD data. (b) Monomer consumption. (c) Vinyl concentration. (d) Active site concentration. Line and point styles represent the same as in Figure 1.

Figure S4. Summary of monomer consumption data for experiments performed at $[\text{cat}]_0 = 5.0 \ \text{mM}$, $[\text{act}]_0 = 5.5 \ \text{mM}$, $[1\text{-hexene}]_0 = 500 \ \text{mM}$, and $25 \ ^\circ \text{C}$. 
Figure S5. Model prediction of a data set at \([\text{cat}]_0 = 5.0 \text{ mM}, [\text{act}]_0 = 5.5 \text{ mM}, [\text{1-hexene}]_0 = 500 \text{ mM},\) and 25 °C. The data correspond to the turquoise data of Figure S4. Red represents a model with the Scheme 2 parameters equal to the average values in Table 2, but with the percent of catalyst participation = 42.6%. (a) MWD curves correspond to ▬20 s, ▪▪▪30 s, and ···157 s. (b) Monomer consumption data.

Figure S6. Model prediction of a data set at \([\text{cat}]_0 = 5.0 \text{ mM}, [\text{act}]_0 = 5.5 \text{ mM}, [\text{1-hexene}]_0 = 500 \text{ mM},\) and 25 °C. Red represents the Scheme 2 model with parameters equal to the average values in Table 2, but with the percent of catalyst participation = 46.5%. (a) MWD curves correspond to ▬30 s and ▪▪▪90 s. (b) Vinylidene groups are represented by filled circles and the solid line. Vinylene groups are represented by open circles and the dashed line.

Figure S7 shows several experiments performed at a M:C ratio of 200:1. The blue data represents an experiment performed as a batch scale reaction, while the rest of the experiments were performed in NMR tubes. The black data, which has twice the concentration of precatalyst (and monomer) of the other experiments interestingly does not have twice the slope of the other experiments as would be expected for a reaction that is first-order in monomer. This set of data was modeled in the main text (Figure 6).
Figure S7. Summary of monomer consumption data for experiments performed at M:C ratios of approximately 200:1 and 25 °C. The symbol ● represents experiments with the initial concentrations of [cat]₀ = 2.6 mM catalyst, [act]₀ = 2.6 mM, and [1-hexene]₀ = 500 mM. The symbol ▲ represents the experiment with the initial concentrations of [cat]₀ = 5.0 mM, [act]₀ = 5.5 mM, and [1-hexene]₀ = 1000 mM.

The model developed in the text is compared with these data. Two model predictions appear in Figure S8 along with the experimental data from one trial. In the first model prediction, all rate constants were constrained to the Table 2 values except for the fraction of active catalyst, which was optimized. In the second model prediction, an additional step was taken to try to see if the fit could be improved. The rate constants were allowed to optimize to values within the error limits specified in Table 2. We reason that any set of rate constants within these error bounds will still provide a good fit of the data from which they were optimized. A slight improvement is seen with this technique. For this experiment, the model predicts that 42% of the catalyst participates in the experiment. The Table 2 rate constant values were also used to predict the data of a second experimental trial (Figure S9) In this case, when 37% of the catalyst participates in the reaction the rate constants do not need to be adjusted in order to provide a good model prediction.
Figure S8. Model predictions of data at \([\text{cat}]_0 = 2.6 \text{ mM}, [\text{act}]_0 = 2.6 \text{ mM}, \text{ and } [\text{1-hexene}]_0 = 500 \text{ mM}\) at 25 °C. Red represents the Scheme 2 model with parameters equal to the average values in Table 2, but with the percent of catalyst participation = 44.6%. Blue represents the Scheme 2 model with the parameters optimized within the 95% confidence interval reported in Table 2, but with the percent of catalyst participation = 42.0%. (a) MWD curves correspond to \(-\cdot-\cdot-\cdot\)45 s, \(-\cdot\cdot\cdot\)140 s, and \(-\cdot\cdot\cdot\)360 s. The data correspond to the blue data of Figure S7. (b) Monomer consumption data.

Figure S9. Model prediction of data at \([\text{cat}]_0 = 2.6 \text{ mM}, [\text{act}]_0 = 2.6 \text{ mM}, \text{ and } [\text{1-hexene}]_0 = 500 \text{ mM}\) at 25 °C. The data correspond to the green data in Figure S7. Red represents the Scheme 2 model with parameters equal to the average values in Table 2, but with the percent of catalyst participation = 37.5%. (a) MWD curve corresponds to 375 s. (b) Monomer consumption data.

S7. Catalyst Activation

In this publication, much is made of the idea of having only a fraction of the measured precatalyst actually participating in the catalytic cycle. The reason for a significant loss of catalyst is not yet understood; the measured fraction of catalyst participation does not correspond to initial precatalyst, activator, or monomer concentrations. Among the additional possibilities is that incomplete catalyst activation occurred. This hypothesis was tested.
Figure S10. $^{19}$F NMR spectrum of Zr[tBu-ON$^\text{NMe}_2$O]Bn$_2$/B(C$_6$F$_5$)$_3$ in d$_8$-toluene.

In a nitrogen-filled glovebox, catalyst precursor Zr[tBu-ON$^{\text{NMe}_2}$O]Bn$_2$ (15.0 mg, 0.0195 mmol) and diphenylmethane (9.9 mg, 0.059 mmol) as an internal standard were dissolved in 2 mL d$_8$-toluene in an air tight NMR tube and sealed with a screw-cap septum. The NMR tube was removed from the glovebox atmosphere, and a $^1$H NMR spectrum was taken. The NMR tube was transferred back into the glovebox, and tris(pentafluorophenyl)boron (11.0 mg, 0.021 mmol) in 0.5 mL was added. The NMR tube was removed from the glovebox, and $^{19}$F (Figure S10) and $^1$H NMR spectra were acquired.

Comparing the integration values of the free borane (-128.4 ppm, -143.2 ppm, and -160.6 ppm) to the total integration values of the peaks shown in Figure S10 demonstrates that the percentage
of free borane in solution is 10%. This value is consistent with the amount of excess borane that was used in the experiment. We conclude that all of the catalyst in the solution has been activated. This experiment, however, cannot rule out that when activator and monomer are simultaneously introduced to the precatalyst an unwanted effect occurs that will prevent a portion of the catalyst from activating.

**S8. Kinetic Modeling with 100% Catalyst Participation**

In the main text, it was stated that the mechanism in Scheme 2 could not model the polymerization data of Figure 1 when the initial concentration of catalyst in the model was set equal to the measured precatalyst amount. This section shows why this is the case.

The experimental data displayed in Figure 1 show that the amount of active catalyst measured through NMR is significantly less than the amount of precatalyst measured for the experiment. This presents a difficulty when trying to predict the experimental data with a mechanism that demands 100% of the catalyst to participate in the reaction. It should be noted that due to workup procedures the active site measurements only account for catalyst sites with non-volatile polymer chains, meaning at the time of the quench there must be more than about three monomers inserted for this active site to be counted.

The total amount of active catalyst varies among the three repeats, but the maximum concentration of primary and secondary sites with a chain of at least four monomers is never greater than 47% of the precatalyst. Using the assumption that all of the precatalyst has been activated, at any point during the experiment at least 53% of the catalyst must have three or fewer (possibly zero) monomers. There are three potential forms that this “missing” catalyst can take: pre-initiated catalyst; post-chain transfer yet un-reinitiated catalyst; or catalyst with
polymer chains consisting of only 1, 2, or 3 monomers. The consequences of each of these cases will be examined, and it will become apparent why they are insufficient to describe the data.

For there to be a significant amount of pre-initiated catalyst, the initiation rate must be very small compared with the propagation rate. When initiation is much slower than propagation, a pronounced induction period will be seen in the monomer consumption data. However, the Figure 1 data fail to display the induction period that would signify a slow initiation rate. Therefore, a slow initiation rate by itself cannot predict the data.

If, instead, the reinitiation rate were very small compared with the propagation rate, then as chain transfer begins to take place the amount of active catalyst sites, whether primary or secondary, would decrease from a maximum value approximately equal to the amount of precatalyst for that experiment, at which point the bulk of the catalyst would be awaiting further monomer insertion. Because the active site data shows a maximum value that is less than half of the amount of precatalyst slow re-initiation must be ruled out as the source of the missing catalyst.

If the system has both a slow initiation and a slow reinitiation rate, there may be a set of rate constants that yields a slow increase to the maximum seen in the data followed by a slow decrease that occurs mainly after the final data point. However, while the right combination of rate constants can predict this behavior, the predictions for the MWDs are qualitatively incorrect because their high molecular weight tails of the later time MWDs are too sharp when compared to the data (Figure S11). Therefore this combination of rate constants must also be ruled out as an explanation of the data.
Figure S11. Best fit of the active site and MWD data from Trial 1 in Figure 1. Red represents a model prediction with slow initiation and re-initiation rates compared with the propagation rate. (a) Active site data, where the filled circle represents the total concentration of active sites (primary and secondary). (b) MWD data, where the distribution times are reported in Figure 1.

The final possibility is that a large portion of the catalyst has been initiated (or reinitiated) but has only a short chain attached. For this mechanism to be able to predict a relatively constant amount of active sites, a significant amount of chain transfer must occur for very short chain polymers (oligomers). Yet with a chain transfer rate so large one would not expect any polymer chains to grow as long as 10,000 g mol⁻¹, which is the order of magnitude of the peak molecular weight seen in the data. Even in combination with the two other potential pathways that have been discussed, it is easily seen that the data is not consistent with this catalyst state. In summary, it must be concluded that some fraction of the precatalyst does not participate in the catalysis process at any time during the reaction.

S9. Kinetic Modeling without Recovery Pathway

As outlined in the text, the simplest kinetic mechanism that can model the distinct chemical species seen through experimentation contains monomer misinsertion, chain transfer to vinylidene sites, and chain transfer to vinylene sites in addition to standard propagation. The additional need for a slow initiation rate and a re-initiation pathway can be inferred from thoughtful observation of the data. What is not obvious is the need for a recovery pathway
Scheme 2 is used as a starting mechanism, but without the recovery pathway. The rate constant approximation techniques used in Section S4 can be used in this case as well. In fact, the approximation for $k_{\text{rec}}$ in the text is zero, so the exact same set of rate constants will be used as a starting point for parameter optimization. A weighting scheme giving all data responses equal importance is used first (see Section S3). The model prediction is shown in red in Figure S12. A major problem with this model is that the two MWD predictions late in the experiment are not correctly shaped. An alternative weighting scheme, one that gives increased importance to these two MWDs as well as to the active site data, is used to produce the blue model prediction in Figure S12. Even in this best case, the distribution shapes do not match the data. The high MW tails in the model are significantly steeper than they are in the data. Although graphically a minor point, the shape of the distribution says a great deal about the reactions present during the experiment, and shape discrepancies are judged more severely than position discrepancies. It was found and reported in the main text that the inclusion of the misinsertion pathway provides a correction to the shape of the distributions without sacrificing the good fit seen for the other data responses.

**S10. Mechanism with Monomer-Dependent Vinylene Formation**

Figure 1 presents the best fit of the experimental data using Scheme 2. Alternate reaction schemes were considered that also provided a qualitatively accurate prediction of the data. The most notable alternate reaction scheme is the one which is identical to Scheme 2, but in which vinylene is formed in a bimolecular reaction between a secondary catalyst site and a monomer.
Figure S12. Model prediction of the Trial 1 data of Figure 1 using Scheme 2 but with the recovery pathway excluded. Red represents a model where all data responses are given equal weighting. Blue represents a model where the two late reaction MWDs and the active site data are given increased weighting. (a) MWD data. (b) Monomer consumption. (c) Vinyl concentration. (d) Active site concentration. Line and point styles represent the same as in Figure 1.

The method outlined in Step 3 was followed using the alternate reaction scheme. The best set of parameter values provides the model prediction seen in Figure S13. The rate constant values are given in Table S3. In both cases, the vinylene data can be predicted reasonably well given the right set of rate constants. The major drawback to the alternate mechanism is with the prediction of the secondary active site data (Figure S13f). Given the uncertainty in the data, the alternative mechanism cannot be strictly rejected. However, the Scheme 1 model provides a much better prediction of both primary and secondary active site data, and it has been chosen as the preferred scheme. It is noteworthy that the rate constants in Table S3 do not vary significantly from the corresponding values in Table 2, with the exception of $k_{\text{mis}}$, which was demonstrated to be the least well-known rate constant in the main text.
**Figure S13.** Model prediction of the data from Figure 1 using the Scheme 2 mechanism but with monomer independent vinylene formation replaced by monomer dependent vinylene formation. Colored lines represent the model predictions using the parameters in Table S3. (a-c) MWD data. (d) Monomer consumption. (e) Vinyl concentration. (f) Active site concentration. Line and point styles represent the same as in Figure 1.

**Table S3.** Optimized kinetic parameters for model predictions in Figure S13.

<table>
<thead>
<tr>
<th>Parameter $^a$</th>
<th>Trial 1 (red)</th>
<th>Trial 2 (green)</th>
<th>Trial 3 (blue)</th>
<th>Average $^b$</th>
<th>% Error $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_p$ (M$^{-1}$ s$^{-1}$)</td>
<td>11.95</td>
<td>11.88</td>
<td>11.61</td>
<td>11.81 ±0.18</td>
<td>2%</td>
</tr>
<tr>
<td>$k_{mis}$ (M$^{-1}$ s$^{-1}$)</td>
<td>0.0797</td>
<td>0.0779</td>
<td>0.0755</td>
<td>0.0777 ±0.0021</td>
<td>3%</td>
</tr>
<tr>
<td>$k_{rec}$ (M$^{-1}$ s$^{-1}$)</td>
<td>0.111</td>
<td>0.104</td>
<td>0.097</td>
<td>0.104 ±0.007</td>
<td>7%</td>
</tr>
<tr>
<td>$k_{vinylidene}$ (s$^{-1}$)</td>
<td>0.0142</td>
<td>0.0106</td>
<td>0.0124</td>
<td>0.0124 ±0.0018</td>
<td>15%</td>
</tr>
<tr>
<td>$k_{vinylene}$ (M$^{-1}$ s$^{-1}$)</td>
<td>0.047</td>
<td>0.054</td>
<td>0.057</td>
<td>0.053 ±0.005</td>
<td>10%</td>
</tr>
<tr>
<td>$k_i$ (M$^{-1}$ s$^{-1}$)</td>
<td>0.214</td>
<td>0.173</td>
<td>0.152</td>
<td>0.180 ±0.032</td>
<td>18%</td>
</tr>
<tr>
<td>Fract of active catalyst</td>
<td>0.439</td>
<td>0.443</td>
<td>0.455</td>
<td>0.446 ±0.008</td>
<td>2%</td>
</tr>
</tbody>
</table>

$^a$k$^{\text{reinitiation}}$ was fixed at 20 M$^{-1}$ s$^{-1}$. $^b$Uncertainty represents a 95% confidence interval using the Student’s t-distribution. $^c$% Error = uncertainty/average.
References
